

Solid State physics

✓ Define crystal substance and amorphous substance.

→ Solids are divided into two categories:

① Crystalline Solids: → In this state, the solids are characterized by perfect or nearly perfect, periodicity of atomic structure.

e.g. NaCl, KCl etc.

② Amorphous: → In such solids, though the atoms or molecules are strongly bounded yet there is hardly any geometrical regularity or periodicity in the way in which the atoms are arranged in space.

e.g. glass, pitch etc.

✓ Distinguish between crystalline and amorphous solid.

Crystalline Solid

① Crystalline solids have a regular arrangement of particles.

e.g. NaCl, KCl etc.

✓ ② They have sharp melting point

✓ ③ They have different physical properties such as refractive index, electrical conductivity, thermal conductivity in different directions i.e. crystalline substance are anisotropic.

Amorphous Solid

① Amorphous solids have a completely random particles arrangement.

e.g. pitch, glass etc.

✓ ② They have no sharp melting point.

✓ ③ Amorphous solids are isotropic. They have their physical properties same in all directions.

\* Why most of the solids are crystalline in nature.

→ For most solids the crystalline state is the natural one since the energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms.

Some important definitions:

Array The arrangement of atoms in a plane or in space is called array of atoms. The array of atoms in plane is called plane lattice and array of atoms in space is called space lattice.

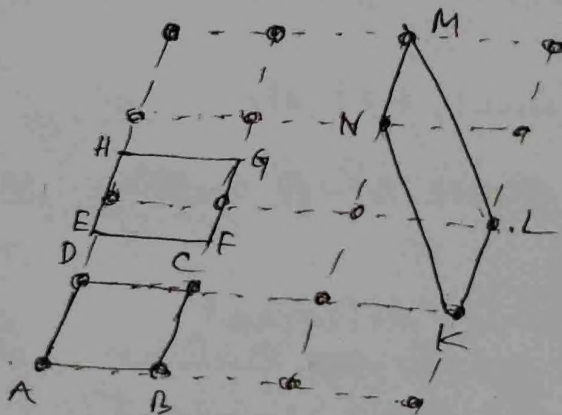
OR

Crystal lattice In a crystalline substance the atoms are regularly arranged. The periodic arrangement of atoms in a crystal is called the lattice/crystal lattice.

It may be plane lattice or space lattice.

\* Unit cell The fundamental elementary pattern of minimum number of atoms, molecules or group of molecules which represent fully all the characteristics of the crystal is known as unit cell. //

The choice of unit cell is by no means unique.  
for example EFGH, ABCD, KLML all are unit cell.



\* Primitive cell It is a type of unit cell which consists only one lattice point at corners and a minimum volume unit.

ABCD and KLML are primitive cell but EFGH non-primitive unit cell. //



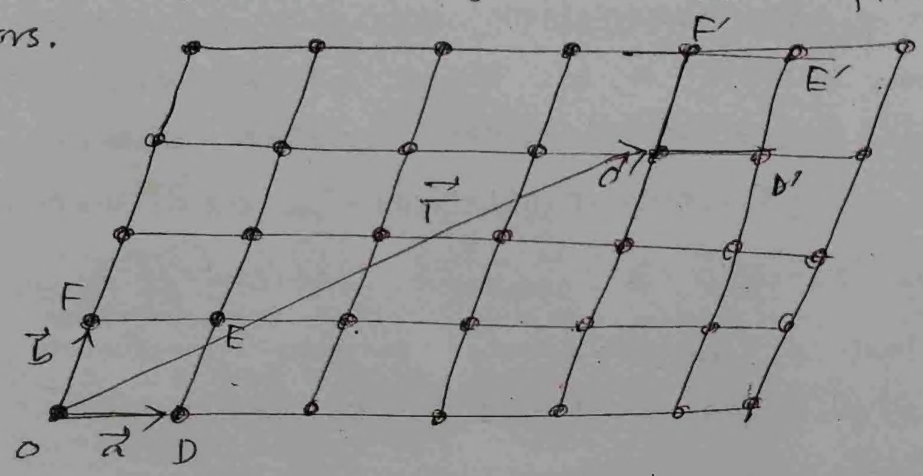
Parallelopiped formed by lattice points only at their corners are called primitive cells.

**Basis** the structure of crystals can be described in terms of a lattice with a group of atoms attached to each lattice point. the group of atom is called the basis.))

A crystal structure is formed by the addition of a basis to every lattice point. i.e lattice combined with a basis creates a crystal structure.

∴ Lattice + Basis = crystal structure.))

**Crystal Translation vector** → In order to represent lattice point in space, a co-ordinate system is required. All the lattice points in space can be generated by translating three non-coplanar unit vectors.



Any the vector  $\vec{a}$  and  $\vec{b}$  (in two dimension) are called translation vector. When a parallelogram is repeatedly translated by the vectors  $\vec{a}$  and  $\vec{b}$  corresponding to  $\vec{OB}$  the pattern may be reproduced.

e.g: If the vector  $\vec{a}$  is translated by  $4\vec{a}$  and vector  $\vec{b}$  by  $3\vec{b}$  the parallelogram  $ODEF$  is translated and repeated as parallelogram  $OD'E'F'$

Here 
$$\vec{T} = 4\vec{a} + 3\vec{b}$$

in general 
$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c} \text{ (in 3d)}$$

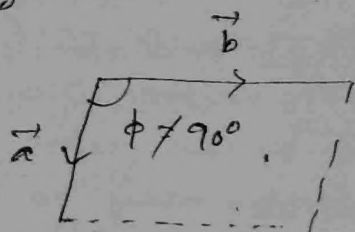
Q/ Can a unit cell be Primitive?

→ A Primitive cell is a type of unit cell which contains lattice points at corners only and is a min. volume cell. A unit cell is a conventional cell which may be equal to a primitive cell or a multiple of it. Thus unit cell can be primitive.

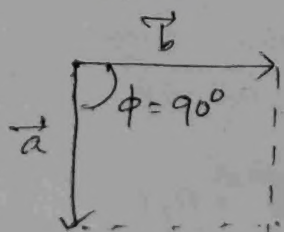
Q/ What is Bravais lattices? Discuss Bravais lattices in two dimensions and draw the different types.

→ There is no natural restriction on lengths  $a, b$  of translation vectors or on  $\phi$ , the angle between them. An unlimited number of lattices is possible. But the requirement that a lattice should be invariant under a rotation operation  $\frac{2\pi}{n}$ ; (where  $n=1, 2, 3, 4$  or  $6$ ) or under the mirror operation places restriction on the primitive translation vectors  $a, b$ . These lattices thus obtained are special type of lattices called Bravais lattices. There are five Bravais lattices in two dimension.

① Oblique lattice: A general lattice is known as oblique lattice. An oblique lattice is shown in fig. 1 where  $|\vec{a}| \neq |\vec{b}|$  and  $\phi \neq 90^\circ$ . The conventional cell is parallelogram.



② Square lattice: A square lattice is shown

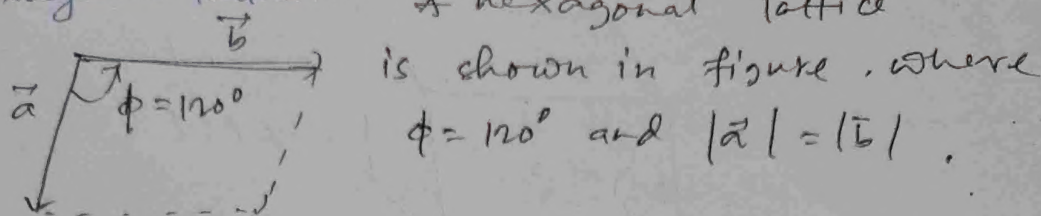


in figure. where  $\phi = 90^\circ$  and  $|\vec{a}| = |\vec{b}|$ .

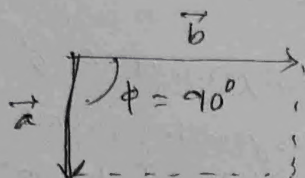


③ Hexagonal lattice: → a hexagonal lattice

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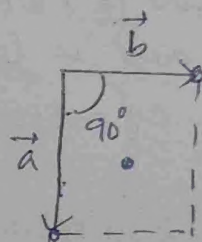
④ Primitive rectangular lattice: → Here  $\vec{a} \neq \vec{b}$ ,  $\phi = 90^\circ$



⑤ centred rectangular lattice: →

Here  $|\vec{a}| \neq |\vec{b}|$  and  $\phi = 90^\circ$ .

a) b, this is invariant under inversion operation.



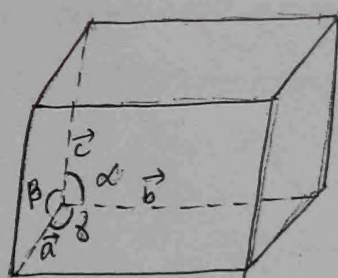
✓ Discuss Bravais lattice in three dimensions and draw the different types.

→ In three dimensions, point symmetry groups requires fourteen different lattice types - one special (triclinic) and thirteen special, collectively called as Bravais lattices. Thus there are only fourteen ways of arranging points in space lattices such that all the points have exactly the same environment.

These fourteen types of lattice are conventionally grouped into seven crystal systems according to seven types of conventional unit cells: they are,

i) Triclinic or Asymmetric System: → In this system of crystal neither the three crystallographic axes are equal,  $a \neq b \neq c$ , nor the three angles are equal  $\alpha \neq \beta \neq \gamma$ , more over none of the angles being right angle.

e.g.  $K_2Cr_2O_7$ ,  $H_3BO_3$ .



$$a \neq b \neq c$$

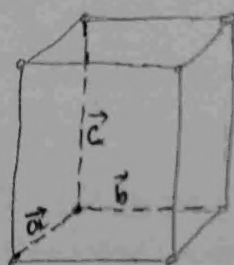
$$\alpha \neq \beta \neq \gamma$$

TRICLINIC

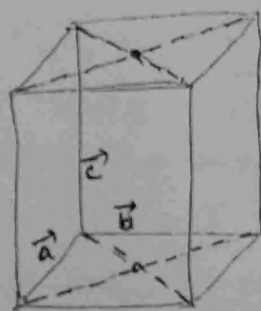
(ii) Monoclinic or monosymmetric system :- In this type of crystals, the crystallographic axes are unequal ( $a \neq b \neq c$ ) one axis is  $\perp^n$  to the other two axes i.e. ( $\alpha = \gamma = 90^\circ$ ,  $\beta \neq 90^\circ$ )

e.g - Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )

Monoclinic lattices may be simple or base-centred as shown in fig. below.



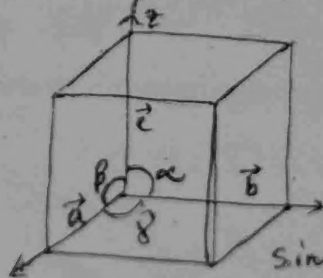
Simple (P)



Base-centred (C)

(iii) Regular or cubic system :- In this the cube system, the crystals are made up of three equal axes at right angles to each other i.e.  $a = b = c$ , and  $\alpha = \beta = \gamma = 90^\circ$  - these crystals have three types of lattice depending upon the shape of unit cells. They are -

a) Simple - cubic - In simple cubic, the particles are only at the corners of the cube



$$a = b = c$$

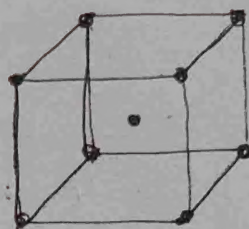
$$\alpha = \beta = \gamma = 90^\circ$$

Simple



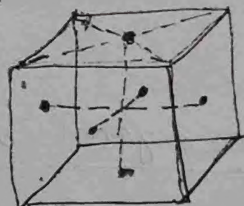
ii) Body centred :- (1)

In body centred the particles are at the corners as well as at the centre of the cube.



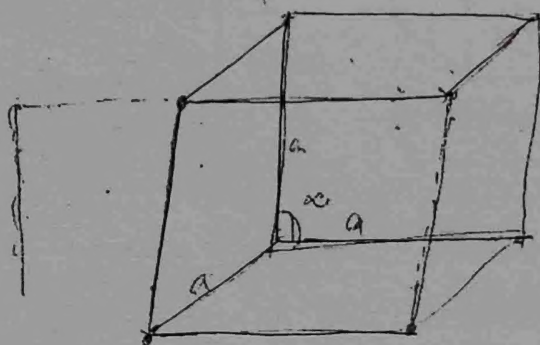
body-centred.

iii) face centred (F) :- In this case the particles are at the corners as well as the centre of each of the face of the cube.



The examples of cubic crystals are :-  
Diamond, Zinc sulphide, etc.

④ Trigonal or Rhombohedral system :- In this system the crystals are made up of three equal axes i.e.,  $a = b = c$  with angles  $\alpha = \beta = \gamma \neq 90^\circ$ . Quartz and calcite are examples of this system.

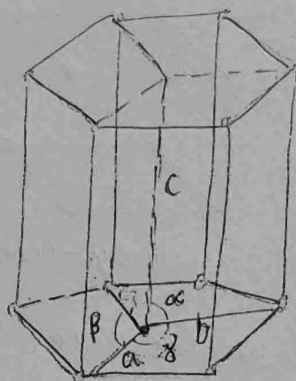


Primitive.

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

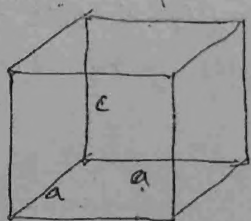
⑤ Hexagonal :- The Hexagonal system has eight faces. the two equilateral axes are equal ( $a = b$ ) and intersects at an angle of  $\gamma = 120^\circ$ . The vertical axis is of different length ( $c \neq a$  or  $b$ ) at right angle to the equilateral axis  $\alpha = \beta = 90^\circ$ . The example of this systems Zincite ( $ZnO$ ), Ice ( $H_2O$ ) etc.



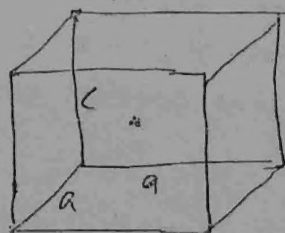
$$\gamma = 120^\circ$$

Simple Hexagonal.

⑥ Tetragonal System → In this system, the three axes are right angles to each other ( $\alpha = \beta = \gamma = 90^\circ$ ) and the two lateral axes are equal. The crystal is characterized by a four fold or tetragonal axis of symmetry.  
 e.g. - ordinary white tin, and indium.



Primitive

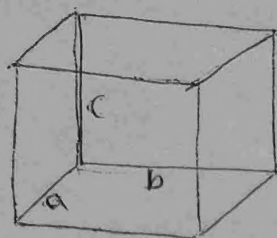


Body-centred

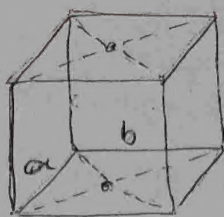
⑦ Orthorhombic System → This system includes the crystals in which crystallographic axes are unequal ( $a \neq b \neq c$ ) but they are at right angles to each other ( $\alpha = \beta = \gamma = 90^\circ$ ). These crystals have three types of lattice depending upon the shape of the unit cell. They are →

- (a) Simple (P).
- (b) Body-centred (I).
- (c) Body-centred (I).
- (d) Face-centred (F).

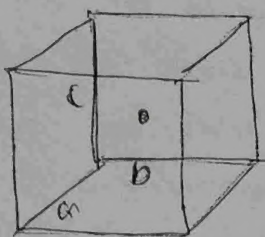




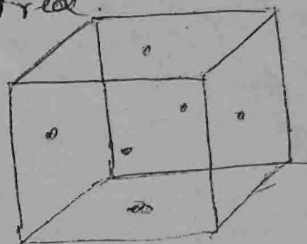
P



C  
Base - centred



I  
Body - centred



F  
Face - centred

### Orthorhombic

\* Lattice symbols atoms  
 → P - primitive - It has 1 only ~~one~~ at the corners of the parallelepiped

C - Base centred - It has extra atoms at the center of the base.

I - Body centred

F - Face centred

Question: Explain the terms — i) Atoms per unit cell. ii) Coordination Number (iii) Atomic radius. (iv) Atomic packing fraction.

Calculate their values for a simple cubic (SC), Face centred - cubic (FCC), Body centred cubic (BCC)

→ Atoms per unit cell →

(a) An atom lying at the corner of a cubic unit cell is shared equally by 8 unit cell and therefore count for  $\frac{1}{8}$ th of an atom.

(b) An atom lying completely within a unit cell belongs wholly to that cell.

(c) An atom lying on the surface of a unit cell belongs equally to two unit cells as one half for that particular cell.

(d) An atom lying at one edge of a unit cell is equally shared by four unit cells and therefore counts one quarter ( $1/4$ ) of an atom for unit cell.

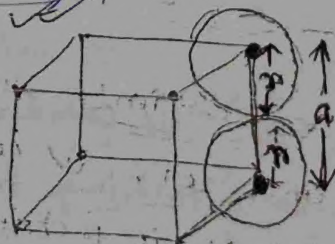
Defn Co-ordination number  $\rightarrow$  the co-ordination number is defined as the number of equidistant neighbours that an atom has in the given structure,

Defn Atomic radius  $\rightarrow$  The atomic radius is the half of the distance bet<sup>n</sup> the centres of two neighbour atoms.

Defn Atomic packing fraction  $\rightarrow$  It is the ratio of the vol<sup>m</sup> of the atoms occupying the unit cell to the vol<sup>m</sup> of the unit cell relating to the structure of the crystal.

(A) Simple cubic cell :-

In this structure the atoms are situated at the corners of the cube touching each other along the edges. Each atom is surrounded by 6 nearest neighbours, so that the co-ordination no. is 6.



From fig.  $2r = a$

$$\Rightarrow r = a/2$$

$\therefore$  Atomic radius  $r = a/2$ , where  $a$  is the



cube edge length  $a$  eg. NaCl, KCl etc

The no of atoms per unit cell is

$$\left[ 8 \times \frac{1}{8} \right] = 1$$

$$\text{Vol}^n \text{ of unit cell} = a^3$$

$$\text{Vol}^m \text{ of the atoms in the unit cell} = \frac{4}{3} \pi \left( \frac{a}{2} \right)^3$$

$\therefore$  Packing fraction,

$$f = \frac{\text{Vol}^m \text{ of atoms in a cell}}{\text{Vol. of a. cell}}$$

$$= \frac{\frac{4}{3} \pi \left( \frac{a}{2} \right)^3}{a^3} \times 100\%$$

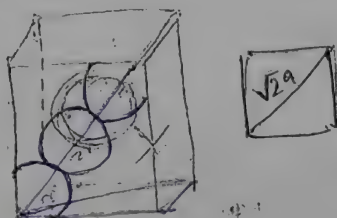
$$= \frac{\pi}{6} \times 100\%$$

$$= 52\%$$

⑧ Body Centred cubic (BCC)

The unit cell is cubic and consists of one atom at each corner and one atom at the centre of the cube. Each atom has only 8 nearest neighbours.

eg. example, Li, Na, K etc has BCC structure.



$$\text{Total no. of atom in BCC cube} = \left( \frac{1}{8} \times 8 + 1 \right)$$

$$= 2$$

$$\text{co-ordination number} = 8$$

$$\text{Atomic radius:— From fig } (\sqrt{2}a)^2 + a^2 = (4r)^2$$

$$\Rightarrow 3a^2 = 16r^2$$

$$\Rightarrow r = \frac{\sqrt{3}a}{4}$$

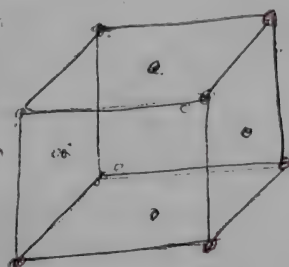
$$\therefore \text{packing fraction } f = \frac{2 \times \frac{4}{3} \pi \left( \frac{\sqrt{3}a}{4} \right)^3}{a^3} \times 100\%$$

$$= \sqrt{3} \frac{\pi}{8} \times 100\%$$

$$= 68\%$$

✓ Face centred cubic (FCC) structure:→

It is cubic and consists of one atom at each corner of the cube and one atom at the centre of each face.



FCC cell.

Each atom has 12 nearest neighbours.

$\therefore$  co-ordination no = 12

Elements possessing FCC structure are Cu, Ag, Au, etc.

Each corner atom is equally shared by 8 surrounding cubes and each of the face centred atoms is equally shared by two cubes.

$\therefore$  total number of atom in FCC cell

$$= \left[ 8 \times \frac{1}{8} \right] + \left[ 6 \times \frac{1}{2} \right]$$

$$= 4 \text{ atoms.}$$

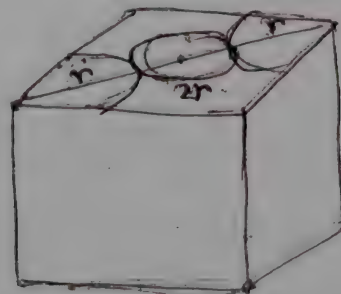
Atomic radius!

$$(4r)^2 = a^2 + a^2$$

$$\Rightarrow 16r^2 = 2a^2$$

$$\Rightarrow r^2 = \frac{a^2}{8}$$

$$\Rightarrow r = \frac{a}{2\sqrt{2}} = \frac{\sqrt{2}a}{4}$$





∴ Packing fraction

(t)

$$P = \frac{4 \times \frac{4}{3} \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} \times 100\%$$

$$= 73.3\%$$

Question - Show that for a cubic lattice lattice constant  $a$  is given by,

$$a = \left[ \frac{M_A n}{N_A \rho} \right]^{1/3}$$

→ (Let us consider a cubic lattice of lattice constant  $a$ . Let if  $V$  be the vol<sup>n</sup> of unit cell then  $V = a^3$ .)

Let  $n$  be the no. of atoms per unit cell and  $\rho$  be the density of the crystal material

$$\therefore \text{mass of the unit cell} = \rho a^3 \quad \text{--- (1)}$$

Let atomic wt. of the material is  $M_A$  and  $N_A$  is the Avogadro's number.

$$\therefore \text{Mass of single atom} = \frac{M_A}{N_A} \quad \checkmark$$

$$\text{And mass of } n \text{ atoms} = n \cdot \frac{M_A}{N_A} \quad \text{--- (2)}$$

$$\text{clearly, } \rho a^3 = n \frac{M_A}{N_A}$$

$$\Rightarrow a^3 = \frac{M_A n}{N_A \rho}$$

$$\Rightarrow a = \left[ \frac{n M_A}{\rho N_A} \right]^{1/3}$$

$\rho a^3$   $\rho a^3$  Proved

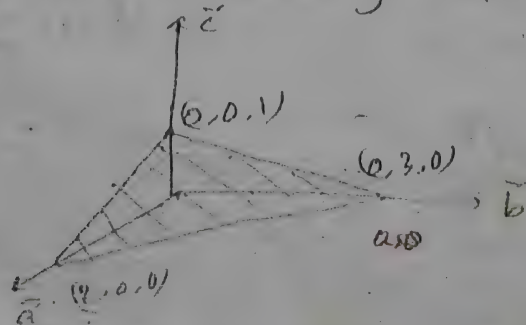
Crystal planes are represented in space by Miller indices:

(2011) A crystal is made up of a large number of parallel equidistant planes (passing through the lattice points) called the lattice planes. The lattice planes can be chosen in a various numbers of different ways. The perpendicular <sup>distance</sup> between adjacent planes is called interplanar spacing. (Miller proposed a method to designate a plane in a crystal using three indices  $(h, k, l)$  these are called Miller indices. Miller indices are the three smallest possible integer which have the same ratio as the reciprocal of the intercept of the plane concerned on the lattice axes.)

Question: What do you mean by Miller indices of a set of atomic planes in a crystal? (2008). Sketch the  $(100)$ ,  $(110)$ ,  $(111)$  planes in a cubic crystal.

Ans (ii) Draw a diagram to indicate the  $(111)$  plane of a simple cubic crystal. (2001)

→ Miller indices: The position and orientation of a crystal plane are determined by three points in the plane provided the points are not collinear. If each point lies on a crystal axis, the plane can be specified by giving the position of the points along the three axes in terms of lattice constant.



$$\frac{a}{1}, \frac{b}{1}, \frac{c}{1}$$

$$\frac{1}{a}, \frac{1}{b}, \frac{1}{c}$$

$$h:k:l = 1:1:1$$

$$(111)$$



of the points have the coordinates  $(0, 3, 0)$ ,  $(0, 0, 1)$  <sup>2.35</sup> and  $(2, 0, 0)$  relative to axis vectors from same origin as shown in the above fig. the plane may be specified by these numbers  $(2, 3, 1)$

In crystal structure analysis, it is more useful to specify the moment of a plane in accordance with the following rules:-

(i) First the intercepts of the plane on the crystal axes  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  in terms of lattice constants are obtained.

(ii) taking the reciprocals of these numbers or their smallest ratio is obtained and the result is denoted by  $(hkl)$  enclosed in parentheses.

The three integers  $hkl$  are called Miller indices.

(100) Plane:-

The face ABGF cuts x-axis at A and is parallel to y and z-axes. when a face is parallel to an axis, intercept on that axis is infinite.

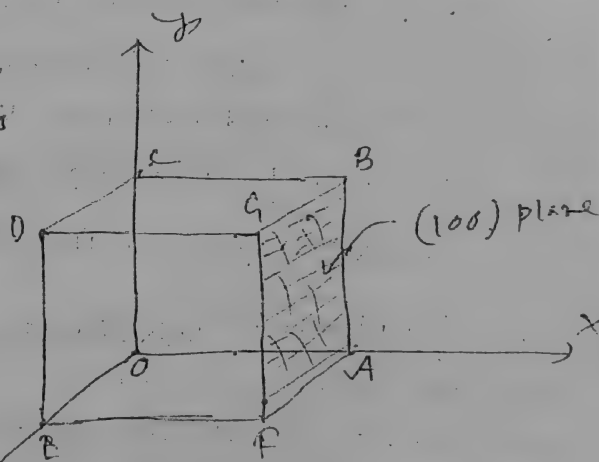
Let the sides of

the cube is one unit in length then the intercepts made by this plane on these axes are in the ratio  $1 : \infty : \infty$

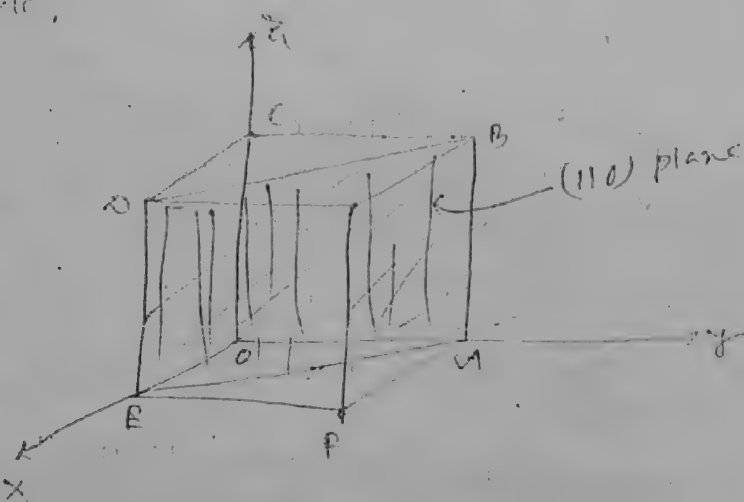
As the miller indices are reciprocal of these intercepts, the reciprocals are

$$\frac{1}{1} : \frac{1}{\infty} : \frac{1}{\infty} = 1 : 0 : 0$$

This face is called cubic face and is expressed as (100) face.



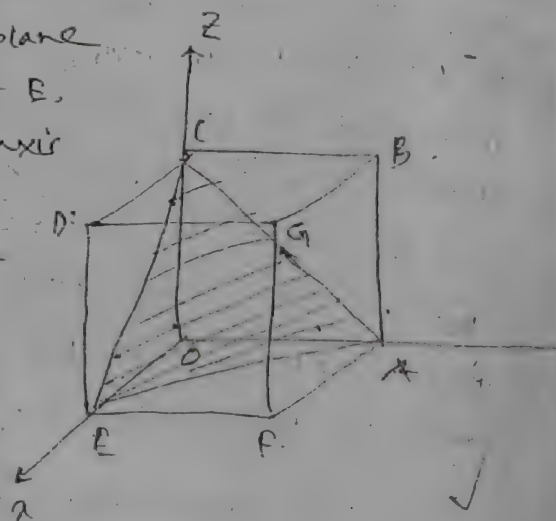
(110) plane — The plane ABDE cuts x-axis at E and y-axis at A and is parallel to z-axis.



When the face is parallel to an axis, intercept on that axis is infinite. Let the sides of the cube is one unit in length then the intercepts made by this plane on three axes are in the ratio  $1:1:\infty$

As the miller indices reciprocals of these intercepts, the reciprocals are  $\frac{1}{1} : \frac{1}{1} : \frac{1}{\infty} = 1:1:0$ . This face is called cubic face and is expressed as  $(110)$ .

(111) plane — The plane ACE cuts x-axis at E, y-axis at A and z-axis at C. Let the sides of the cube is one unit in length, then the intercepts made by this plane on the three axes are in the ratio  $1:1:1$ .



As the miller indices are reciprocal of these intercepts, the reciprocals are  $\frac{1}{1} : \frac{1}{1} : \frac{1}{1} = 1:1:1$ . This face is called cubic



face and is expressed as (111) face.

Question:- write down the Miller indices for the planes with intercepts of  $(6a, 2b, 3c)$  and  $(a, 2b, c)$  . P.T.O.

— (i) intercepts are  $(6a, 2b, 3c)$

∴ Reciprocal of the numbers representing intercepts  $= \frac{1}{6} : \frac{1}{2} : \frac{1}{3}$

$$= 1 : 3 : 2$$

∴ Miller indices =  $(132)$

(ii) intercepts are  $(a, 2b, c)$

∴ their reciprocal  $= \frac{1}{1} : \frac{1}{2} : \frac{1}{1}$

$$= 2 : 1 : 2$$

∴ Miller indices =  $(212)$

$$\begin{array}{r} \frac{1}{6} \cdot \frac{1}{2} \cdot \frac{1}{3} \\ \hline 1 \cdot 3 \cdot 2 \\ \hline \frac{1}{1} \cdot \frac{1}{2} \cdot 1 \\ \hline 2 \cdot 1 \cdot 2 \end{array}$$

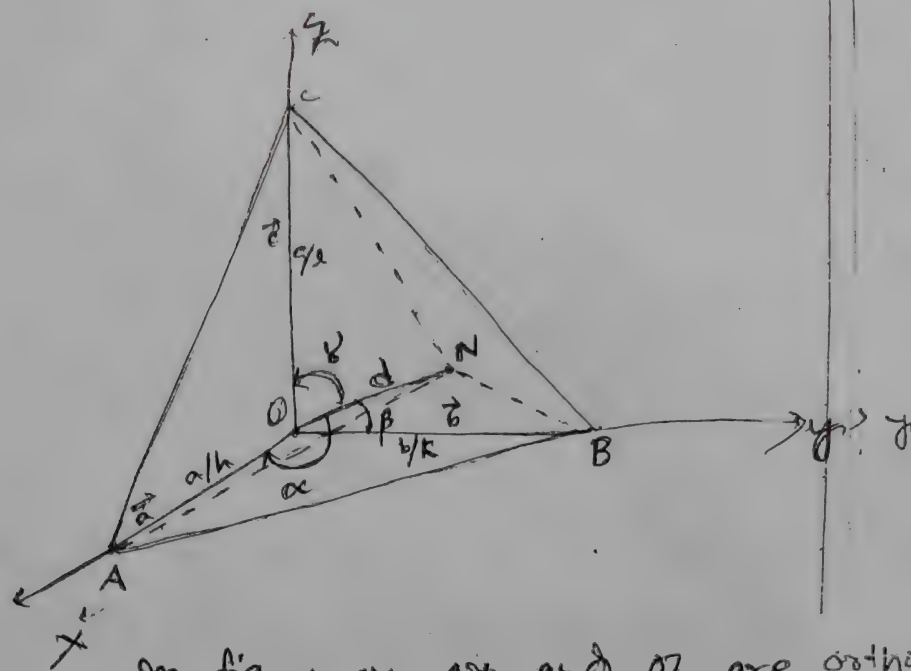
(2011) Question:- Derive the expression for the inter planar separation of the  $(hkl)$  plane of a simple cubic lattice.

OR

Show that the interplanar spacing .

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{ for cubic crystal.}$$

→ we shall derive a formula for the spacing bet<sup>n</sup> two parallel planes in a given simple cubic lattice in which co-ordinate axes are orthogonal.



In fig :  $ox$ ,  $oy$  and  $oz$  are orthogonal axes. the <sup>origin</sup>  $O$  is taken at any lattice point. We consider any set of crystal planes defined by the Miller indices  $(hkl)$

Let the reference plane passes through the origin and the next plane cuts the intercepts  $a/h$ ,  $b/k$ ,  $c/l$  on  $x$ ,  $y$ ,  $z$  axes respectively.

A normal  $ON$  is drawn to the plane  $ABC$  from the origin  $O$ . the length of this normal from the origin to the plane will be the distance bet<sup>n</sup> adjacent planes.

We have to find the expression for

$d (= ON)$  in terms of  $a, b, c$  and  $h, k, l$ .

from fig: we get-

$$d = \frac{a}{h} \cos \alpha = \frac{b}{k} \cos \beta = \frac{c}{l} \cos \gamma$$

~~we have~~

where  $\alpha = \angle NOA$

$\beta = \angle NOB$

$\gamma = \angle NOC$  are direction cosines.



$$\cos \alpha = \frac{dh}{a} ; \cos \beta = \frac{dk}{b} ; \cos \gamma = \frac{dl}{c}$$

Squaring and adding we get,

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = d^2 \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

$$\Rightarrow 1 = d^2 \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

$$\Rightarrow d^2 = \frac{1}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

$$\Rightarrow d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

For a cubic system,  $a = b = c$ .

$$\therefore d = \frac{1}{\frac{1}{a} \sqrt{h^2 + k^2 + l^2}}$$

$$\Rightarrow d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

This is the expression for the interplanar distance.))) ✓ ✓ ✓

Ques NaCl crystal has a cubic structure. If its density is  $2.163 \text{ gm/cm}^3$  and its molecular weight is  $58.45 \text{ g}$ . Calculate the lattice constant. (2011)

→ According to the given problem

$$\rho = \text{density of NaCl} = 2.163 \text{ g/cm}^3$$

$$M = \text{molecular wt. of NaCl} = 58.45 \text{ g}$$

$$N = \text{Avogadro's number} = 6.02 \times 10^{23}$$

$$n = \text{no. of molecules per unit cell} = 4$$

(for f.c.c structure)

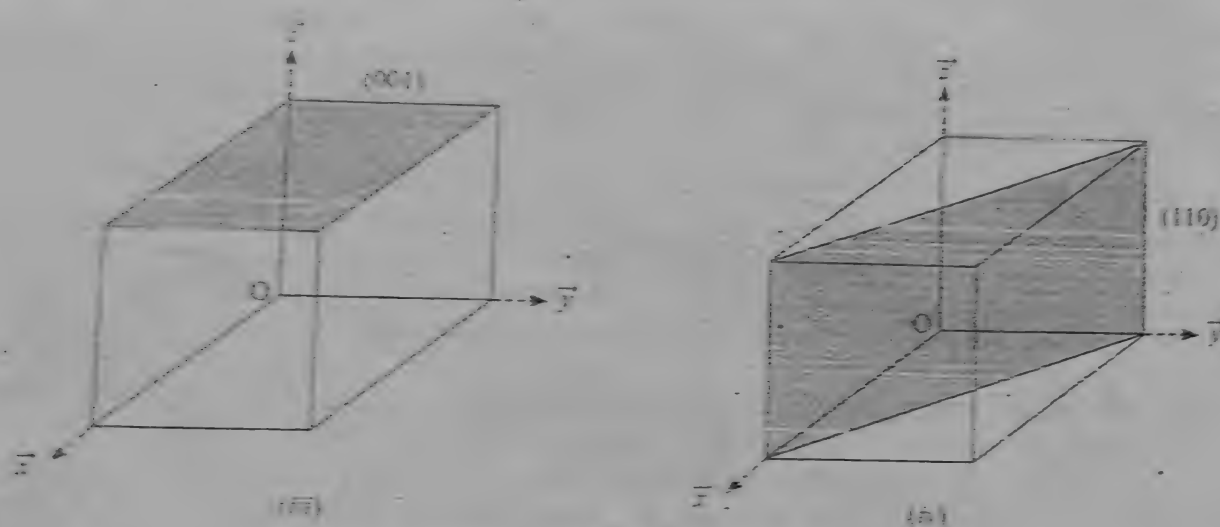


Fig 1.32

- (i)  $(101)$  plane. The  $(101)$  plane is parallel to  $y$ -axis and has an intercept 1 on  $x$ -axis as well as on  $z$ -axis. Fig. 1.32 (v)
- (ii)  $(011)$  plane. The  $(011)$  plane is parallel to  $x$ -axis and has an intercept 1 on  $y$ -axis as well as on  $z$ -axis. Fig. 1.32 (vi)

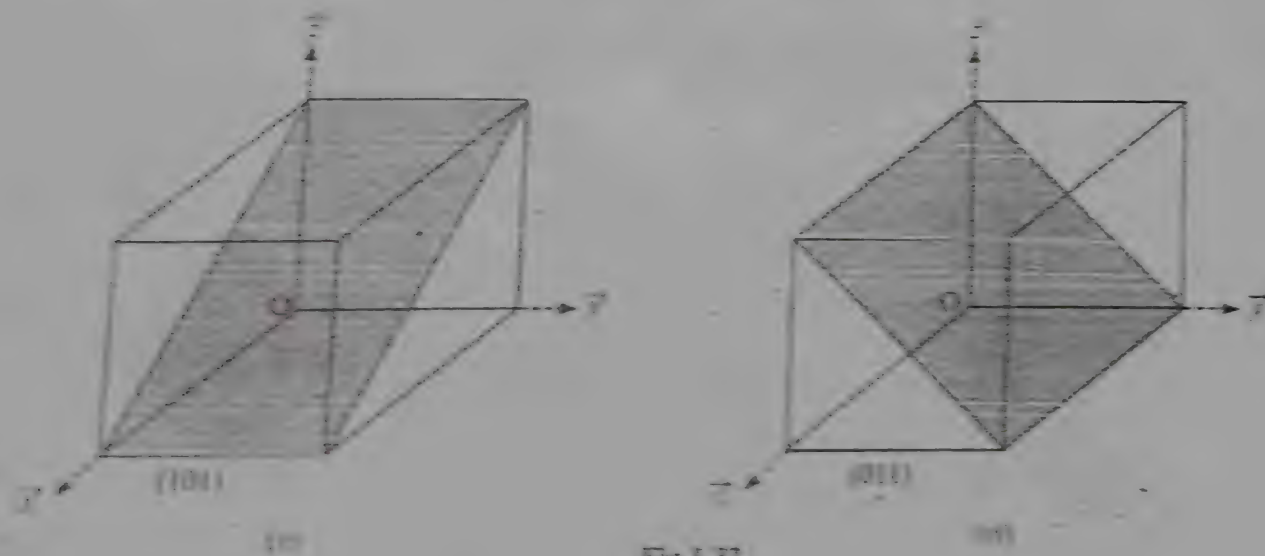


Fig 1.32

- (iii)  $(111)$  plane. The  $(111)$  plane has intercept 1 along each of the three axis  $x$ ,  $y$  and  $z$ . Fig. 1.32 (vii)
- (iv)  $(200)$  plane. The  $(200)$  plane has intercept  $\frac{1}{2}$  on the  $x$ -axis and lies in the  $y$ - $z$  plane. Fig. 1.32 (viii)



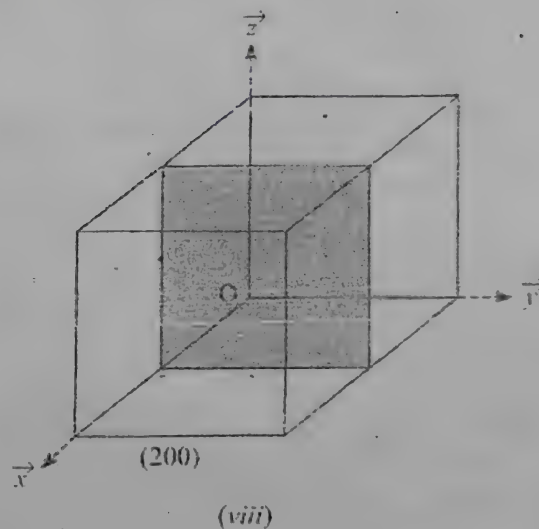
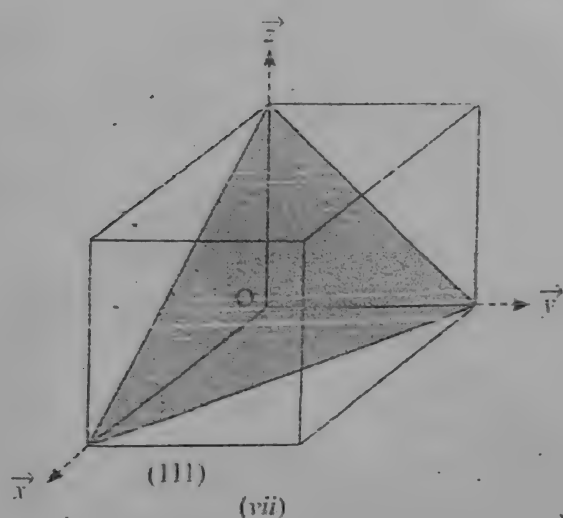


Fig 1.32

(ix) **(020) plane.** The (020) plane has intercept  $\frac{1}{2}$  on the y-axis and lies in the  $x-z$  plane. Fig. 1.32 (ix)

(x) **(002) plane.** The (002) plane has intercept  $\frac{1}{2}$  on the z-axis and lies in the  $x-y$  plane. Fig. 1.32 (x)

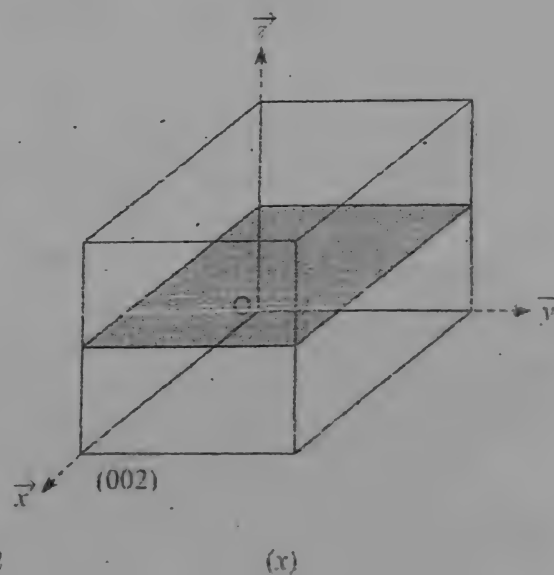
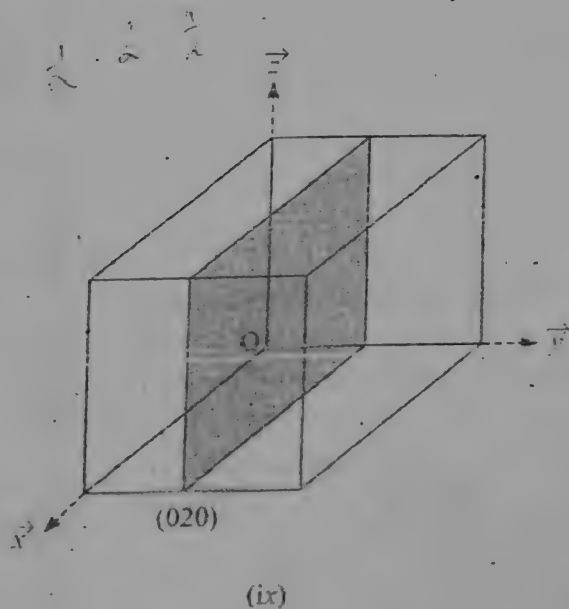


Fig 1.32

(xi) **(201) plane.** The (201) plane has intercept  $\frac{1}{2}$  on the x-axis, is parallel to y-axis and has an intercept 1 on the z-axis. Fig. 1.32 (xi)

(xii) **(112) plane.** The (112) plane has intercept 1 each on x-axis and y-axis and intercept  $\frac{1}{2}$  on the z-axis. Fig. 1.32 (xii)

Question what is atomic scattering factor and Geometrical scattering factor.

Sol: → Atomic Scattering factor → the atomic scattering factor  $f$  is defined as the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by ~~an~~ a single electron localised at a point.

$$\therefore f = \frac{\text{Amplitude of radiation scattered from an atom}}{\text{Amplitude of radiation scattered from an electron.}}$$

Geometrical Structure factor → It is defined as the ratio of the amplitude of the wave scattered by an entire unit cell to the amplitude of the wave scattered by a single point electron for the same wavelength at the origin. origin.)

(Different types of crystal bonding)

Question: Explain the term bonding. What are the different kind of bonding in crystals.

Bonding: (the ability to hold the atoms or ions together is called bonding. (The basic requirements of all types of bonding is that all bound system should have minimum energy in their stable form.))

Types of Bonding → the individual atoms of a crystalline solid are held together as one system with different types of bonds existing between them. These bonds are classified into five types:

- ✓ (a) Ionic Bonding: (Due to transfer of valence electron)  
e.g: NaCl, LiF etc
- ✓ (b) Co-valent Bonding: (sharing of valence electrons)  
e.g: diamond, SiC etc.
- (c)



✓ Van der waal bonding: (electrons remain associated with original molecules)

e.g: Solid argon.

① Hydrogen Bonding. e.g. ice.

② metallic Bonding. Cu, Ag, Fe.

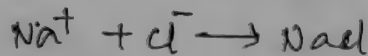
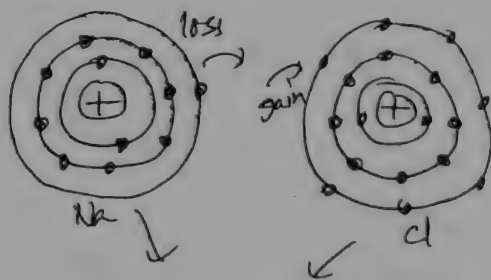
(Here valence electrons are essentially free).

✓ Question what is ionic bonding? State the properties of ionic crystals.

→ Ionic bonding: (When the bonding between two atoms occur due to the ~~at~~ actual transfer of valence electrons are known as covalent ionic ~~as~~ bonding.)

this type of bonding arises from the transfer of one or more electrons from an electropositive element to an electronegative element. The electropositive atoms have a low ionisation energy\* and the electronegative elements are of high electron affinity\*.

✓ Example: NaCl. The Na atom loses the only valence electron in its outermost valence orbit and becomes positive. The Cl atom is short of one electron in its outermost valence orbit. It therefore takes up the electron given by Na atom and forms NaCl crystal.



✓ ~~\*~~ the energy required to remove an electron from an atom.

✓ ~~\*~~ Energy given up when a neutral atom gains an electron and becomes a negative ion.

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Properties of ionic crystal  $\rightarrow$  Properties of ionic crystals are:

- ✓ ① The ionic crystals are strong, hard and brittle.
- ✓ ② The ionic crystals are generally insulators. Their electrical conductivity is very low at ordinary temperatures but increases with increase of temperature.
- ✓ ③ Ionic crystals are normally transparent to visible light, while
- ④ Their dielectric constant changes with the frequency of A.C. applied.
- ✓ ⑤ They are generally brittle in nature and could not be drawn into sheets or wire.

Note  $\rightarrow$  Strong electrostatic forces between positive and negative ions make ionic crystals hard. However, when a shearing force is applied to an ionic crystal the ions tend to slip past one another with relatively more ease, as the ionic bonding is non-directional. A stage is reached when strong repulsive forces cause a fracture of the crystal, i.e., the crystal is brittle.

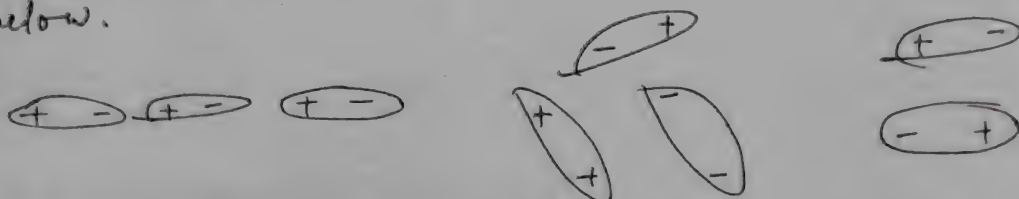
Question Explain the Van der Waals Bonding in crystal:  
Explain the Van der Waals bonds are weakest. Write down physical characteristics of inert gas crystals.

✓ Van der Waals Bonding  $\rightarrow$  The atoms of inert gas are spherically symmetrical and have no valence electrons as their outermost electron orbits are completely filled. They are, therefore, incapable of forming any bond. Also certain organic molecules and molecules containing atoms of halogens - oxygen attain inert gas configuration. However, these molecules condense to solid and liquid. To explain this, Van der Waals suggested some type of attractive force between these molecules and inert gases.



(Van der Waals attraction between two molecules, at a distance  $r$  apart, is proportional to  $r^{-7}$  i.e. it is very short range force.

~~In most~~ Some polar and non-polar molecules tend to align themselves with ends having opposite kind of charge and attract each other as shown below.



→ ~~Van~~ Van der Waals attraction is very weak as it is proportional to  $r^{-7}$  ( $r =$  distance bet<sup>n</sup> the atoms). As such it is significant only for molecule very close together. This is a short range force falling rapidly as the atoms separate. Because of these Van der Waals bond is very weak.

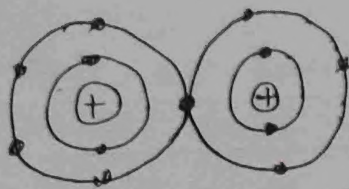
### Property

- ✓ ① The inert gas crystals have low melting and low boiling points.
- ✓ ② They easily change their state with a small amount of thermal energy.
- ✓ ③ the inert gas crystal are brittle and lack strength.
- ✓ ④ the inert " " have very high ionisation energy.

Question Discuss covalent bonding in crystals. State the properties of covalent crystals.

covalent bonding  $\Rightarrow$  The types of bonding resulting from sharing of one or more electrons by the atoms is known as covalent bonding.

e.g.: diamond, Silicon, Germanium etc.



## \* Properties of covalent bonding:-

- ① These substances are made up of individual covalent molecules with weak intermolecular forces.
- ② These substances are generally insoluble in ordinary liquids but soluble in ether and benzene etc.
- ③ Covalent crystals are very hard.
- ④ Their dielectric constant is independent of applied field.
- ⑤ The conductivity of covalent crystal varies over a wide range.

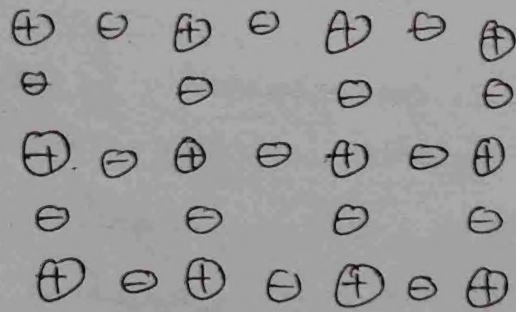
Question Discuss metallic bonding. Write down the properties of metallic bonding.

→ In case of metals the metallic metal the ionisation energy is low. They have valent valency orbitals and have a few valency electrons as compared to the no. of valency orbitals. Thus in the atom of metals, the electron in the outermost orbitals are loosely bound and are called free electrons. or one or two such electron can be detached from the parent atom due to the attraction of adjacent atomic cores. The remainder portion of the atom  $\oplus$  which is positively charged sphere is called a kernel. The free electrons are mobile in nature and move freely from one kernel to another kernel in the lattice. Thus the crystal lattice may be pictured as an arrangement of positive ions immersed in a sea of mobile electrons.



✓  
The bond thus formed between the metal atoms is known as metallic bond as shown below.

Hence metallic bond may be defined as a result of simultaneous attraction of an electron by two or more than two positive ions of the metal.



metallic Bonding.

\* Properties of metallic bonding:

✓ ① They are good conductors.

✓ ② Heat is produced in the metal when an electric current is passed.

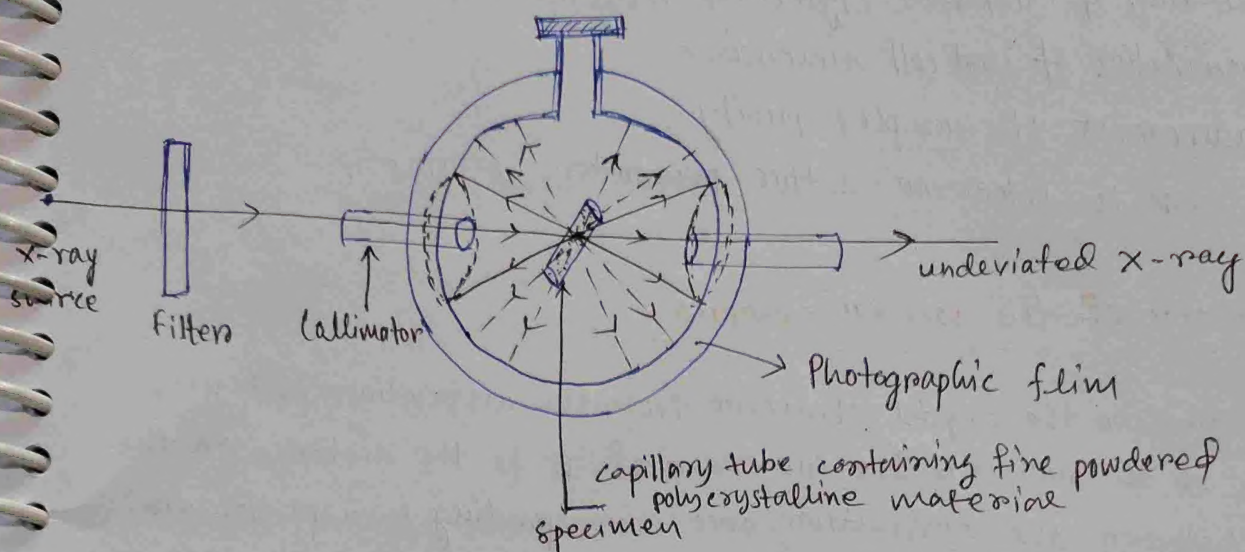
✓ ③ The electrical resistance increases with the heating of metals,

✓ ④ metals have high tensile strength,

✓ ⑤ They have high thermal and electrical conductivity



## Powders Method of X-ray Diffraction by Crystals



The method was devised by Debye and Scherrer in 1916 to determine the structure of finely powdered polycrystalline materials. Finely powdered polycrystalline material is kept inside a capillary tube. A narrow beam of monochromatic X-rays is allowed to fall on the capillary tube. In finely powdered polycrystal material specimen there are many crystals and we have different value of  $\theta$ . X-rays are diffracted only when Bragg's law eq<sup>n</sup>  $2d \sin \theta = n\lambda$  is satisfied.

The beam of X-rays are made monochromatic using a filter. A photographic film is used to receive the diffracted X-rays.

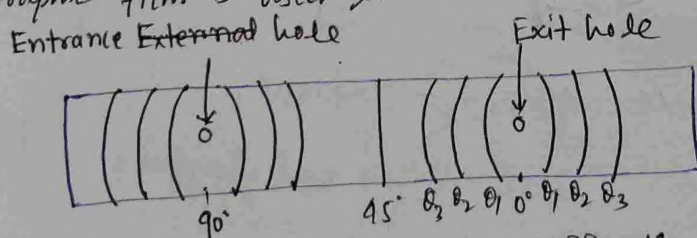


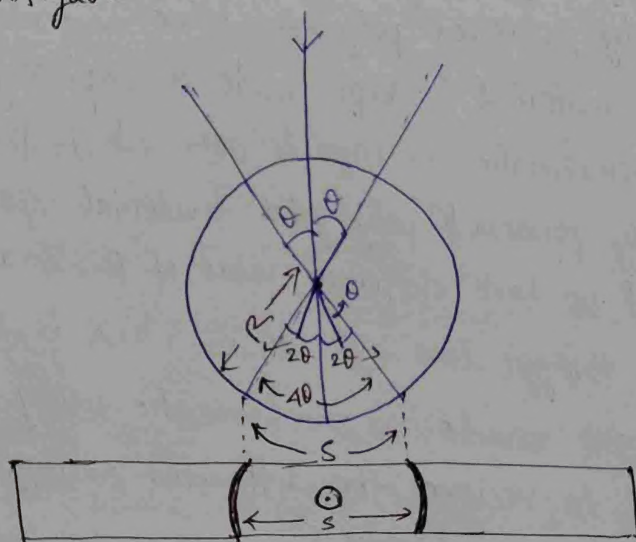
Fig: Arrangement of lines in Diffraction pattern.

### Advantages :-

- i) Identification of unknown crystalline material.
- ii) Determination of unit cell dimensions.
- iii) Measurement of sample's purity.
- iv) It helps to determine lattice parameters  $a, b, c$ .

### # Diameter of the powder camera

To determine the crystal structure from the diffraction pattern, let  $R$  be the radius of the camera and  $S$  be the distance on the film between the diffraction arcs corresponding to a particular plane, then full opening angle of the corresponding cone as shown in figure below.



From the figure, we have  $4\theta = \frac{S}{R}$  radians.  
 $= \frac{180}{\pi R} S$  degrees.

$$\therefore \frac{180}{\pi} = 57.3$$

can be  $\therefore 4\theta = 57.3 \frac{S}{R}$  degrees.

The calculation made simply by taking  $R = 57.3$  mm or a multiple of that because then the glancing angle can be directly calculated. If we take  $R = 57.3$  mm, then  $\boxed{\theta = \frac{S}{4} \text{ mm}}$

This is why the diameter of the powder camera is 57.3 mm or a multiple of that.